(19) Europäisches Patentamt
Eur pean Patent Office
Office européen des brevets

(11) EP 0 705 803 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
10.04.1996 Bulletin 1996/15

(21) Application number: 95916005.2

(22) Date of filing: 19.04.1995

(51) Int. Cl.[6]: C04B 35/486, A61C 7/14, B02C 17/20

(86) International application number: PCT/JP95/00762

(87) International publication number:
WO 95/29141 (02.11.1995 Gazette 1995/47)

(84) Designated Contracting States:
CH DE DK FR GB IT LI NL SE

(30) Priority: 22.04.1994 JP 107636/94
17.03.1995 JP 86509/95

(71) Applicant: SHINAGAWA REFRACTORIES CO., LTD.
Tokyo 100 (JP)

(72) Inventors:
- NAKAYAMA, Susumu
Kurashiki-shi Okayama 710 (JP)
- ICHIMORI, Terumitsu
Urawa-shi Saitama 338 (JP)
- MINO, Tadahiro
Bizen-shi Okayama 705 (JP)
- AYUZAWA, Nobuo
Kakogawa-shi Hyogo 675 (JP)

(74) Representative: Hansen, Bernd, Dr. Dipl.-Chem. et al
Hoffmann, Eitle & Partner,
Patentanwälte,
Arabellastrasse 4
D-81925 München (DE)

(54) ZIRCONIA SINTER, PROCESS FOR PRODUCING THE SAME, GRINDING PART MATERIAL, AND ORTHODONTIC BRACKET MATERIAL

(57) A zirconia-based sinter stabilized with a rare earth metal oxide is provided which has high fracture toughness properties, is excellent in mechanical strength and thermal stability, and contains a boron compound. A process for producing the sinter and a grinding part material and a bracket material for dental correction both constituted of said zirconia-based sinter are also provided.

Specifically, a zirconia-based sinter comprising ZrO_2 as the main component, one or more rare earth metal oxides (R_2O_3) selected from Yb_2O_3, Er_2O_3, Ho_2O_3, Y_2O_3, and Dy_2O_3, and a boron compound [or a boron compound and Al_2O_3 and/or SiO_2], wherein R_2O_3/ZrO_2 (molar proportion) is from 1.3/98.7 to 2/98, excluding 2/98, and the content of boron components is from 0.05 to 8% by mole in terms of B_2O_3 [or in addition thereto the content of Al_2O_3 is from 0.1 to 5% by mole and/or the content of SiO_2 is from 0.05 to 1.5% by mole]. A grinding part material and a bracket material for dental correction both constituted of the zirconia-based sinter.

EP 0 705 803 A1

Descripti n

TECHNICAL FIELD

The present invention relates to a zirconia-based sinter and a process for producing the same, and to a grinding part material and a bracket material for dental correction both constituted of said zirconia-based sinter. More particularly, this invention relates to a zirconia-based sinter stabilized with a rare earth metal oxide which sinter has high fracture toughness properties, is excellent in mechanical strength and thermal stability, and contains a boron compound, a process for producing said sinter, and a grinding part material and a bracket material for dental correction both constituted of said zirconia-based sinter.

BACKGROUND ART

In recent years, a zirconia (ZrO_2)-based sinter is extensively used as a constituent material of, e.g., ceramic scissors and medical materials taking advantage of its toughness, mold extrusion dies taking advantage of its lubricity, heat-insulating engine parts taking advantage of its heat-insulating properties and thermal expansion characteristics, or oxygen sensors and fuel cells taking advantage of its oxygen ion conductivity. It is known that of such sinters the zirconia-based sinters containing a rare earth metal oxide as a stabilizer have exceedingly high fracture toughness properties as compared with other ceramics. Products taking advantage of this property are being developed enthusiastically. For example. attention is focused on use as a grinding part material, e.g., a grinding medium for use in the mixing or grinding of ceramic materials, metal powders, food-related substances, or the like. Also attracting attention is use as a bracket material for dentition correction which is superior in aesthetic property to bracket materials made of metal, polymer, etc., and combines high strength and toughness.

By the way, the fracture toughness properties of a zirconia-based sinter containing a rare earth metal oxide as a stabilizer tend to decrease in proportion to the amount of the stabilizer and to sintering temperature. For example, it is known that zirconia-based sinters having a stabilizer content lower than 2% by mole show excellent fracture toughness properties.

Consequently, the tendency described above indicates that a zirconia-based sinter having high fracture toughness properties can be obtained if a raw material containing a stabilizer in an amount smaller than 2% by mole (hereinafter abbreviated simply as "low-mole") is used and can be sintered at a low temperature.

However, it is extremely difficult to sinter zirconia with a low-mole stabilizer. In addition, zirconia-based sinters containing a rare earth metal oxide as a stabilizer generally have a drawback that they are susceptible to deterioration during long-term aging in a low-temperature region (the deterioration being caused by the transition of tetragonal crystals, which constitute a metastable phase at ordinary temperature among the crystal phases of the zirconia-based sinter, to monoclinic crystals, which constitute a stable phase, and by the development of minute cracks within the sinter as a result of a volume expansion accompanying the phase transition). In particular, aging in water or steam at 100 to 300°C is a cause of considerable deterioration, and zirconia-based sinters stabilized with a low-mole stabilizer are more apt to undergo such a phenomenon.

The prior art techniques have therefore had a problem that a zirconia-based sinter having high toughness properties is difficult to produce. Even if a zirconia-based sinter having high toughness is produced, this kind of highly tough zirconia-based sinters have drawbacks of poor thermal stability in a low-temperature region and impaired product reliability and, hence, have a problem that the applications thereof are considerably limited.

Grinding part materials comprising a zirconia-based sinter excellent in strength and wear resistance have been proposed so far (see, e.g., examined Japanese patent publication No. 20587/1990). However, since these prior art zirconia-based sinters undergo a considerable decrease in strength upon long-term standing at around 100 to 300°C and the rate thereof (rate of strength decrease) is exceedingly high especially in a water or steam atmosphere, the sinters raise difficulties, for example, in a wet grinding step using water as solvent or in the case where grinding part materials are washed with water etc., before being subjected to a drying step at a high temperature (around 200°C). As a sinter which eliminates such a problem, a zirconia-based sinter containing both a boric acid compound (e.g., B_2O_3) and Al_2O_3 and/or SiO_2 [and further containing a rare earth metal oxide in an amount of 2% by mole or larger] has been proposed in unexamined published Japanese patent application No. 239662/1994 and others.

Such zirconia-based sinters show improved thermal stability. However, since these zirconia-based sinters contain 2% by mole or more rare earth metal oxide as a stabilizer, they neither show excellent fracture toughness properties comparable to that of zirconia-based sinters having a stabilizer content lower than 2% by mole, nor satisfy all the properti s including fracture toughness properties and wear resistance.

On the other hand, bracket materials for dentition correction which comprise a zirconia-based sinter as a material similar to teeth in appearance and color tone and excellent in strength and toughness have been proposed in French patent No. 2,559,059, unexamined published Japanese patent application No. 21857/1990, unexamined published Japanese patent application No. 280864/1992, and others. For example, in unexamined published Japanese patent appli-

cation No. 21857/1990 is described use of a zirconia-based sinter as a bracket material for dentition correction which sinter is a "so-called partially stabilized zirconia" partially stabilized with Y_2O_3 or the like. In unexamined published Japanese patent application No. 280864/1992 is described use of a partially stabilized zirconia as a bracket material for dentition correction which zirconia contains a colorant comprising erbium oxide, praseodymium oxide, and iron oxide and is very similar in color tone to human teeth.

However, such prior art zirconia-based sinters also undergo a considerable decrease in strength upon long-term standing at around 100 to 300°C, and the rate thereof (rate of strength decrease) is exceedingly high especially in a water or steam atmosphere. The decrease of strength proceeds even at lower temperatures.

Medical materials including bracket materials for dentition correction raise difficulties, because these materials are especially frequently subjected at a high-temperature (around 100 to 300°C) to cleaning with water as a solvent, disinfection, sterilization, or another treatment. As a sinter which eliminates such a problem, a zirconia-based sinter containing both a boron compound (e.g., B_2O_3) and Al_2O_3 and/or SiO_2 [and further containing a rare earth metal oxide in an amount of 2% by mole or larger] has been proposed in Japanese patent application No. 169453/1994 and others. Such zirconia-based sinters show improved thermal stability. However, since these zirconia-based sinters contain 2% by mole or larger rare earth metal oxide as a stabilizer, they neither show excellent fracture toughness properties comparable to that of zirconia-based sinters having a stabilizer content lower than 2% by mole, nor satisfy all the properties including fractur toughness properties.

The present invention has been achieved in view of the drawbacks and problems described above. Objects of the present invention are as follows:

- the first object is to provide a zirconia-based sinter which contains a low-mole rare earth metal oxide as a stabilizer, can be produced through sintering at a relatively low temperature, and is excellent in thermal stability and fracture toughness properties, and to provide a process for producing the same;
- the second object is to provide a grinding part material which employs the zirconia-based sinter described above and a zirconia-based sinter obtained by the process for producing the same; and
- the third object is to provide a bracket material for dentition correction which likewise employs the zirconia-based sinter described above and a zirconia-based sinter obtained by the process for producing the same.

DISCLOSURE OF THE INVENTION

The zirconia-based sinter according to the present invention is characterized as being obtained by sintering a composition comprising ZrO_2 as the main component, a rare earth metal oxide (R_2O_3) in a given range, and a boron compound in a given range (or a boron compound in a given range and Al_2O_3 and/or SiO_2 in a given range). Thus, a zirconia-based sinter excellent in thermal stability and fracture toughness properties is provided.

Further, the process according to the present invention for producing a zirconia-based sinter is characterized as comprising preparing a raw-material blend by a chemical synthesis method, such as the neutralizing coprecipitation method, the hydrolytic method, the alkoxide method, or the like, or by the oxide-mixing method so as to result in a given raw-material composition, calcining the blend at a given temperature (500 to 1,200°C), subjecting the calcination product to a pulverization step to obtain a raw-material powder having a given specific surface area (which is 3 m^2/g or larger when the blend was obtained by a chemical synthesis method, or is 10 m^2/g or larger when the blend was obtained by the oxide-mixing method), subsequently molding the raw-material powder, and then sintering the molding at a given temperature (1,300 to 1,650°C). Thus, sintering can be conducted at a relatively low temperature, and a zirconia-based sinter excellent in thermal stability and fracture toughness properties can be obtained.

Furthermore, the grinding part material and the bracket material for dentition correction according to the present invention are characterized as employing the zirconia-based sinter described above and a zirconia-based sinter obtained by the production process described above which zirconia-based sinters each has given property values.

BEST MODES FOR CARRYING OUT THE INVENTION

Detailed explanations are given below in order on the zirconia-based sinter of the present invention, the process for producing the same, and the grinding part material and the bracket material for dental correction both employing the zirconia-based sinter.

First, the zirconia-based sinter according to the present invention is explained in detail.

As stated above, the zirconia-based sinter according to the present invention contains ZrO_2 as the main component and employs as a stabilizer one or more rare earth metal oxides selected from the group consisting of Yb_2O_3, Er_2O_3, Ho_2O_3, Y_2O_3, and Dy_2O_3 (in this specification, the rare earth metal oxides are abbreviated as "R_2O_3"). (Although Tm_2O_3 and Lu_2O_3 are also usable, Tm_2O_3 and Lu_2O_3 are highly expensive to make zirconia products poorly competitive in the market).

The sinter may also contain a rare earth metal oxide other than the aforementioned R_2O_3, as long as the content thereof is 0.5% by mole or lower based on ZrO_2-R_2O_3; this sinter is also included in the present invention. In this case, the presence of a rare earth metal oxide other than the aforementioned R_2O_3 does not bring about a noticeable change in mechanical strength as long as the content thereof is 0.5% by mole or lower based on ZrO_2-R_2O_3. However, contents thereof not lower than 0.5% by mole are undesirable in that mechanical strength decreases.

The proportion of this stabilizer (R_2O_3) is characterized in that the molar proportion thereof to ZrO_2 (R_2O_3/ZrO_2) is from 1.3/98.7 to 2/98, excluding 2/98. If the molar proportion of the stabilizer (R_2O_3) to ZrO_2 is below 1.3/98.7, the desired sinter is difficult to obtain because tetragonal crystals of ZrO_2 are hardly maintained at ordinary temperature and the transition of the tetragonal crystals to monoclinic crystals results in a volume change, which is accompanied by cracking. In short, such proportions are undesirable because the effect of the stabilizer is insufficient (see "Composition No. 18" in Tables 1 and 2 given later and "Composition No. 44" in Tables 4 and 6). On the other hand, molar proportions of the stabilizer (R_2O_3) to ZrO_2 of 2/98 and higher are undesirable in that although a zirconia-based sinter excellent in sintering property and mechanical strength is obtained, this sinter hardly has the high fracture toughness properties desired in this invention and, hence, the high-toughness zirconia-based sinter of the present invention cannot be obtained (see "Composition No. 20" in Tables 1 and 3 given later and "Composition No. 46" in Tables 4 and 6). Therefore, in the zirconia-based sinter according to the present invention, the molar proportion of the R_2O_3 to ZrO_2 (R_2O_3/ZrO_2) is desirably from 1.3/98.7 to 2/98, excluding 2/98, with the preferred range thereof being from 1.5/98.5 to 2/98, excluding 2/98.

The zirconia-based sinter according to the present invention is further characterized in that it contains a boron (B) component therein. This boron component is an additive capable of improving the thermal stability of zirconia-based sinters. However, if the amount of boron (B) is smaller than 0.05% by mole in terms of B_2O_3, it does not produce the effect of improving thermal stability (see "Composition Nos. 1 and 2" in Tables 1 and 2 given later and "Composition Nos. 27 and 28" in Tables 4 and 5). In contrast, sinters having a boron amount exceeding 8% by mole are undesirable in that the boron compound tends to reduce rather than increase the thermal stability of the sinters (see "Composition No. 5" in Tables 1 and 2 given later and "Composition No. 31" in Tables 4 and 5). Therefore, the amount of boron (B) is from 0.05 to 8% by mole, preferably from 0.2 to 5% by mole, in terms of B_2O_3.

In the present invention, a compound of boron may be used as an additive (boron source) for incorporating a boron component. Examples thereof include boron oxide, boron nitride, boron carbide, or compounds of Zr, Al, Si, Yb, Er, Ho, Y, or Dy with boron (B).

Al_2O_3 and/or SiO_2 may be added to the zirconia-based sinter according to the present invention for the purpose of further improving thermal stability, improving sintering properties, etc. The sinter desirably has an Al_2O_3 amount in the range of from 0.1 to 5% by mole (preferably from 0.3 to 2% by mole) and an SiO_2 amount in the range of from 0.05 to 1.5% by mole (preferably from 0.1 to 0.5% by mole). In sinters having an Al_2O_3 amount smaller than 0.1% by mole or an SiO_2 amount smaller than 0.05% by mole, the effect of addition of the individual elements is not produced. On the other hand, zirconia-based sinters containing Al_2O_3 in an amount exceeding 5% by mole are undesirable in that fracture toughness properties decrease in proportion to the amount of Al_2O_3 (see "Composition No. 13" in Tables 1 and 2 given later and "Composition No. 39" in Tables 4 and 5). Further, zirconia-based sinters containing SiO_2 in an amount exceeding 1.5% by mole are undesirable in that the thermal stability obtained by the effect of boron incorporation described above tends to be reduced (see "Composition No. 15" in Tables 1 and 2 given later and "Composition No. 41" in Tables 4 and 5).

In the zirconia-based sinter according to the present invention, the incorporation of Al_2O_3 or SiO_2 produces the effects thereof not only in the case of incorporating three components of "B_2O_3-Al_2O_3-SiO_2", but also in the case of incorporating two components of "B_2O_3-Al_2O_3" or "B_2O_3-SiO_2" as long as the addition amounts thereof are within the respective ranges specified above (see "Composition Nos. 6 and 7" in Tables 1 and 2 given later and "Composition Nos. 32 and 33" in Tables 4 and 5). Additives for these (Al source and Si source) may be the oxides of these additive components (Al and Si). Besides these, the elements may also be added in the form of nitride, carbide, hydroxide, or the like to obtain the same effects. All of these are included in the present invention.

The process according to the present invention for producing a zirconia-based sinter is then explained.

First, using a chemical synthesis method, such as the neutralizing coprecipitation method, the hydrolytic method, the alkoxide method, or the like, or using the oxide-mixing method, a raw-material powder is prepared so that the powder has the above-specified raw-material composition concerning ZrO_2, R_2O_3, and a boron compound (and Al_2O_3 and/or SiO_2 according to need). Subsequently, this raw-material powder is calcined in the temperature range of from 500 to 1,200°C. The calcined powder is pulverized and then molded. The molding is subjected to sintering (main burning) in the temperature range of from 1,300 to 1,650°C.

In the production process of the present invention, the calcination at 500 to 1,200°C is intended to homogenize the raw material as much as possible and to cause part of the ZrO_2 to undergo phase transition so as to accelerate sintering in the burning step (main burning step). This calcination is one of the important requisites to the production process of the present invention. The lower limit, 500°C, in the calcination conditions is the minimum temperature at which part of the monoclinic crystals of ZrO_2 can be phase-transferred to tetragonal crystals by calcination. It is generally said that the transfer of monoclinic crystals of ZrO_2 to tetragonal crystals occurs at around 1,170°C. However, adding a stabilizer to ZrO_2 shifts the transition temperature to the lower-temperature side. For example, in compositions containing Y_2O_3

as a stabilizer, the phase transition occurs at a temperature around 800°C. This temperature varies depending on the kind or amount of the stabilizer.

On the other hand, the upper limit of calcination temperature, 1,200°C, is the maximum temperature at which a calcined raw material containing aggregates which are sufficiently pulverizable in a pulverization step can be produced. Raw materials calcined at a temperature exceeding that temperature are undesirable in that aggregates remain after pulverization, which serve as large breaking sites to reduce the strength of the zirconia-based sinter. Therefore, the calcination temperature in the process of the present invention is preferably from 500 to 1,200°C.

The raw material which has undergone calcination should be pulverized because it has aggregated in some degree. The specific surface area of the raw-material powder obtained by this pulverization should be 3 m^2/g or larger when the raw material was obtained by a chemical synthesis method, or should be 10 m^2/g or larger when the raw material was obtained by the oxide-mixing method. The specific surface area thereof is preferably in the range of from 8 to 20 m^2/g when the raw material was obtained by a chemical synthesis method, or in the range of from 15 to 30 m^2/g when the raw material was obtained by the oxide-mixing method. Raw-material powders having a specific surface area smaller than 3 m^2/g in the case where the raw material was obtained by a chemical synthesis method or having a specific surface area smaller than 10 m^2/g in the case where the raw material was obtained by the oxide-mixing method are undesirable in that such powders have poor sintering properties and hardly give a dense sinter. In order to obtain a dense sinter from a raw-material powder whose specific surface area is smaller than 3 m^2/g in the case where the raw material was obtained by a chemical synthesis method or is smaller than 10 m^2/g in the case where the raw material was obtained by the oxide-mixing method, sintering (main burning) should be conducted at a temperature outside the temperature range of from 1,300 to 1,650°C specified in this invention; sintering (main burning) outside that range is undesirable because the problems described later arise. Raw-material powders having too large a specific surface area are not too desirable in that handling thereof is difficult. The upper limit of the specific surface area is about 30 m^2/g with respect to both the chemical-synthesis method and the oxide-mixing method.

In the production process of the present invention, the sintering (main burning) temperature is preferably from 1,300 to 1,650°C as stated above, and especially preferably from 1,350 to 1,500°C. Sintering temperatures lower than 1,300°C are undesirable in that the sintering only gives sinters having impaired mechanical properties, while sintering temperatures exceeding 1,650°C are undesirable in that abnormal growth of crystal grains and other troubles occur and, hence, a highly tough sinter is not obtained.

Further, in the production process of the present invention, when a zirconia-based sinter is produced, in particular, through a pressure sintering treatment, the zirconia-based sinter produced can have an even higher strength. For example, the compacts obtained by CIP molding in Examples given later which compacts gave sinters having a strength of 130 kgf/mm^2 or higher can be made to give sinters with a strength as high as 150 kgf/mm^2 or higher by conducting an HIP treatment.

The grinding part material according to the present invention is then explained.

The grinding part material according to the present invention is characterized in that it employs the above-described zirconia-based sinter according to the present invention and a zirconia-based sinter obtained by the above-described production process according to the present invention, and that the zirconia-based sinter has given property values. Specifically, the grinding part material employs a zirconia-based sinter which has an average grain diameter of 2 μm or smaller and a bulk density of 5.8 g/cm^3 or higher and is less apt to deteriorate in long-term use at a temperature of 100 to 300°C in the air or in water and steam. Zirconia-based sinters having an average grain diameter exceeding 2 μm are undesirable in that they have poor wear resistance and poor thermal stability. On the other hand, zirconia-based sinters having a bulk density lower than 5.8 g/cm^3 are undesirable in that the sinters, when used, e.g., as a grinding medium, show a low grinding efficiency and that the sinters have reduced strength property values. Further, sinters which deteriorate in the air or in water and steam at a temperature in the range of from 100 to 300°C are undesirable in that the deterioration is accompanied by considerable decreases in all kinds of properties including wear resistance, grinding efficiency, and strength properties, so that such sinters are unsuitable, for example, for use in a wet grinding step employing water as solvent or for use in the case where the grinding part material is washed with water or the like and is then subjected to a drying step at a high temperature (around 200°C).

The bracket material for dentition correction according to the present invention is then explained.

The bracket material for dentition correction according to the present invention is characterized in that it employs the above-described zirconia-based sinter according to the present invention and a zirconia-based sinter obtained by the above-described production process according to the present invention, and that the zirconia-based sinter employed contains from 0.0001 to 0.002% by mole Pr_6O_{11} and from 0.01 to 0.2% by mole Er_2O_3 as colorants for enhancing the aesthetic properties of the sinter, has an average grain diameter of 2 μm or smaller and a porosity of 1% or lower, and has the property of being less apt to deteriorate in long-term use at a temperature of 100 to 300°C in the air or in water and steam.

If the amounts of Pr_6O_{11} and Er_2O_3 added as colorants are too small and outside the ranges specified above, the color of the sinter is too white. In contrast, if the amounts thereof are too large and outside those ranges, the sinter has a darker color than teeth. In either case, the bracket material, when bonded to teeth, gives an unnatural feeling because

it differs in appearance and color tone from the teeth. Thus, colorant amounts outside the above specified ranges are undesirable from an aesthetic standpoint.

Average grain diameters exceeding 2 μm are undesirable in the zirconia-based sinter constituting the bracket material for dentition correction according to the present invention, because poor thermal stability results. On the other hand, porosities exceeding 1% are undesirable in that such a sinter does not have a glossy aesthetic appearance and has reduced strength property values. Further, sinters which deteriorate in the air or in water and steam at a temperature in the range of from 100 to 300°C are undesirable in that the deterioration is accompanied by considerable decreases in all kinds of properties including aesthetic properties and strength properties, so that difficulties are encountered when bracket materials for dentition correction comprising such sinters are subjected to washing with water, disinfection, sterilization, or the like particularly at a high temperature (around 100 to 300°C).

The zirconia-based sinter according to the present invention (including the zirconia-based sinter for use as the grinding part material and bracket material for dentition correction according to the present invention) is characterized in that the crystal grains thereof consist mainly of a mixed phase (T+M) made up of tetragonal crystals (T) and monoclinic crystals (M).

Since the zirconia-based sinter according to the present invention contains a stabilizer (R_2O_3) in an amount smaller than 2% by mole, no cubic crystals are present therein, and the crystal grains thereof mostly have a mixed phase (T+M) made up of tetragonal crystals (T) and monoclinic crystals (M). In zirconia-based sinters having such a mixed phase (T+M), an improvement in fracture toughness can be expected and such a tendency is observed. The content of monoclinic crystals in the crystalline phase of a zirconia-based sinter was determined by grinding a surface of the sinter with a #600 diamond wheel, subsequently finishing the ground surface with diamond grains of 1-5 μm to give a mirror surface, analyzing the surface by X-ray diffraction, and calculating the content from the resulting intensity ratios using the following equations (1) to (3).

$$\text{Content of monoclinic crystals } X_M = \frac{I_M(111) + I_M(11\bar{1})}{I_M(111) + I_M(11\bar{1}) + I_{T+C}(111)} \qquad \text{Equation (1)}$$

$$\text{Content of tetragonal crystals } X_T = (100 - X_M) \times \frac{I_T(400) + I_T(400)}{I_T(400) + I_C(400) + I_T(400)} \qquad \text{Equation (2)}$$

$$\text{Content of cubic crystals } X_C = 100 - X_M - X_T \qquad \text{Equation (3)}$$

Further, the average grain diameter for a zirconia-based sinter was determined as follows. A surface of the sinter was finished into a mirror surface in the manner described above, and the surface was etched with hydrofluoric acid. The diameter (d) of a circle equal to a given area (S) containing 50 or more grains on an electron photomicrograph was calculated using the equation $d=(4S/\pi)^{1/2}$. This diameter (d) was determined with respect to three or more fields of view in the same sample, and these diameter values were averaged to obtain the average grain diameter. The sum of the number of grains entirely contained in the given area (S) and a half of the number of grains cut by the periphery of the given area is taken as the number of grains (n) (with respect to this measurement method, see examined Japanese patent publication No. 21184/1986).

In the case of the zirconia-based sinter of the present invention having a specific composition, not only a raw material obtained by a chemical synthesis method, such as the neutralizing coprecipitation method, the hydrolytic method, the alkoxide method, or the like, but also a raw material obtained by the oxide-mixing method, which is relatively inexpensive, can be used to obtain a zirconia-based sinter having excellent thermal stability and high fracture toughness properties.

According to the grinding part material of the present invention which employs an R_2O_3-stabilized zirconia-based sinter containing a boron compound and a sintering aid, that is, according to the grinding part material employing a zirconia-based sinter which has the composition specified in this invention and satisfies average grain diameter and bulk density, a grinding part material is provided which has exceptionally high fracture toughness properties, is excellent in wear resistance and thermal stability, and attains high grinding efficiency.

Furthermore, according to the bracket material for dentition correction of the present invention which employs an R_2O_3-stabilized zirconia-based sinter containing a boron compound and a sintering aid, that is, according to the bracket material for dentition correction employing a zirconia-based sinter which has the composition specified in this invention, contains Pr_6O_{11} and Er_2O_3 as colorants, and satisfies average grain diameter and porosity, a bracket material for dentition correction is provided which shows excellent aesthetic properties during use and has exceptionally high fracture toughness and excellent thermal stability.

The present invention will be explained below in more detail by reference to Examples of the invention along with Comparative Examples, but the invention should not be construed as being limited to the following Examples unless the spirit thereof is departed from.

[EXAMPLE 1 (including COMPARATIVE EXAMPLES)]

Zirconium oxide (ZrO_2), a rare earth metal oxide (R_2O_3: stabilizer), boron oxide (B_2O_3), aluminum oxide (Al_2O_3), and silicon dioxide (SiO_2) were weighed out so as to result in the compositions (Composition Nos. 1 to 26) shown in Table 1 given below. Using ion-exchanged water as solvent, each mixture was kneaded with a rubber-lined ball mill

employing ZrO_2-based balls. Drying was then conducted.

TABLE 1

Composition

Composition No.	Kind of stabilizer	R_2O_3/ZrO_2 (mol%)	Al_2O_3 (mol%)	SiO_2 (mol%)	B_2O_3 (mol%)	Remarks
1	Y_2O_3	1.8/98.2	0	0	0	Comparative Example
2	"	"	1	0.3	0	Comparative Example
3	"	"	0	0	2	Example
4	"	"	0	0	8	Example
5	"	"	0	0	12	Comparative Example
6	"	"	1	0	1	Example
7	"	"	0	0.3	1	Example
8	"	"	1	0.3	0.05	Example
9	"	"	1	0.3	1	Example
10	"	"	1	0.3	12	Comparative Example
11	"	"	0.1	0.3	1	Example
12	"	"	5	0.3	1	Example
13	"	"	10	0.3	1	Comparative Example
14	"	"	1	1.5	1	Example
15	"	"	1	3	1	Comparative Example
16	"	1.5/98.5	1	0.3	1	Example
17	"	1.3/98.7	1	0.3	1	Example
18	"	1/99	1	0.3	1	Comparative Example
19	"	1.9/98.1	1	0.3	1	Example
20	"	2.5/97.5	1	0.3	1	Comparative Example
21	Yb_2O_3	1.8/98.2	1	0.3	1	Example
22	Er_2O_3	"	1	0.3	1	Example
23	Ho_2O_3	"	1	0.3	1	Example
24	Dy_2O_3	"	1	0.3	1	Example
25	$Y_2O_3+Dy_2O_3$	(1+0.8)/98.1	1	0.1	0.5	Example
26	$Y_2O_3+Ho_2O_3$	"	1	0.1	0.5	Example

Subsequently, calcination was conducted at the temperatures shown in Tables 2 and 3 (provided that the Composition No. 19 indicated by "Calcination temperature: 0°C" in Table 3 was not calcined). The calcined powders obtained were pulverized with the same ball mill as that used above for kneading, to such degrees as to result in the specific.

surface areas shown in Tables 2 and 3. An acrylic copolymer resin was added in an amount of 3% by weight, and spray granulation was conducted. The resulting powders were subjected to CIP molding at a pressure of 1,000 kgf/cm², followed by main burning at the temperatures shown in Tables 2 and 3 given below.

With respect to each zirconia-based sinter obtained, "three-point bending strength" measured in accordance with Testing Method for Bending Strength of Fine Ceramics (JIS R1601), "Vickers hardness (JIS R1610)," "fracture toughness value (JIS R1607)" determined by the IF method, and the "thermal stability" of the sinter are shown in Tables 2 and 3. The "thermal stability" of each sinter was judged by placing the sinter in an autoclave to conduct a 200-hour aging test

in 200°C hot water and then examining the sinter for deterioration.

TABLE 2

Production Conditions and Properties

Composition No.	Calcination temperature (°C)	Specific surface area (m^2/g)	Main burning temperature (°C)	Average crystal grain diameter (μm)	Crystalline phase	Bending strength (kgf/mm^2)	Vickers hardness, hardness symbol: HV10	Fracture toughness value MPa√m	Thermal stability	Remarks
1	1000	15	1500	0.7	M+T	32.12	802	4.47	poor	Comparative Example
2	1000	15	1500	0.7	M+T	105.33	1100	12.15	poor	Comparative Example
3	1000	15	1500	0.8	M+T	110.11	1072	11.67	good	Example
4	1000	15	1450	0.6	M+T	107.21	1006	12.74	good	Example
5	1000	15	1500	0.8	M+T	100.05	1011	10.67	poor	Comparative Example
6	1000	15	1500	0.7	M+T	121.34	1102	12.40	good	Example
7	1000	15	1500	0.7	M+T	109.82	1032	11.07	good	Example
8	1000	15	1500	0.7	M+T	102.24	1103	12.44	good	Example
9	1000	15	1500	0.7	M+T	120.83	1069	12.36	good	Example
	1000	6	1500	1.0	M+T	21.67	-	-	poor	Comparative Example
	1000	25	1400	0.6	M+T	98.67	1000	13.11	good	Example
10	1000	15	1450		microcracks were present in the sinter					Comparative Example
11	1000	15	1550	0.7	M+T	107.66	1037	12.25	good	Example
12	1000	15	1500	0.7	M+T	117.51	1234	10.73	good	Example
13	1000	15	1550	0.9	M+T	110.03	1311	6.11	good	Comparative Example
14	1000	15	1500	0.7	M+T	97.89	1088	11.63	good	Example
15	1000	15	1500	0.8	M+T	79.66	1050	10.63	poor	Comparative Example
16	800	15	1500	0.6	M+T	107.67	1031	11.30	good	Example
17	800	20	1500	0.5	M+T	98.99	1002	10.69	good	Example
18	800	20	1500			unsintered				Comparative Example

[note] crystalline phase M: monoclinic phase, T: tetragonal phase.

TABLE 3

Production Conditions and Properties

Composition No.	Calcination temperature (°C)	Specific surface area (m^2/g)	Main burning temperature (°C)	Average crystal grain diameter (μm)	Crystalline phase	Bending strength (kgf/mm^2)	Vickers hardness, hardness symbol: HV10	Fracture toughness value MPa√m	Thermal stability	Remarks
19	1000	12	1500	0.7	M+T	131.69	1180	13.11	good	Example
	500	17	1500	0.6	M+T	130.21	1097	13.50	good	Example
	1200	12	1500	0.7	M+T	123.07	1111	12.78	good	Example
	1400	7	1500	0.8	M+T	11.63	-	-	poor	Comparative Example
	0	17	1500	0.7	M+T	60.10	970	4.11	good	Comparative Example
20	1000	15	1500	0.9	T	131.45	1200	7.10	poor	Comparative Example
21	1000	15	1500	0.7	M+T	121.19	1049	12.63	good	Example
	800	30	1350	0.5	M+T	111.11	1008	13.55	good	Example
	800	15	1700	reaction occurred with the burning table						Comparative Example
	1000	15	1200	0.5	M+T	2.09	-	-	poor	Comparative Example
22	1000	15	1500	0.7	M+T	117.66	1112	11.11	good	Example
23	1000	15	1500	0.7	M+T	90.27	1094	9.74	good	Example
24	1000	15	1500	0.7	M+T	88.40	1095	9.66	good	Example
25	800	12	1550	0.6	M+T	109.00	1088	10.99	good	Example
26	1200	10	1600	0.7	M+T	96.66	1133	10.42	good	Example

[note] crystal phase M: monoclinic phase, T: tetragonal phase

From Tables 2 and 3 given above, it is understood that zirconia-based sinters not only showing high strength and a high fracture toughness value but having satisfactory thermal stability are obtained in Example 1, in which the molar proportion of a stabilizer (R_2O_3) to ZrO_2 is within the range specified in this invention and the compositions contain a

boron compound in a given range (or a boron compound in a given range and Al_2O_3 and/or SiO_2). In contrast, the zirconia-based sinter of the present invention cannot be obtained from the compositions which are outside at least one of the aforementioned given ranges specified in this invention, or from the compositions containing no boron (B) component. For example, Composition No. 18 (R_2O_3/ZrO_2=1/99) as a Comparative Example, which was outside the range "R_2O_3/ZrO_2=1.3/98.7 to 2/98, excluding 2/98" specified in this invention, did not sinter because of the too small stabilizer (Y_2O_3) amount, and Composition No. 20 (R_2O_3/ZrO_2=2.5/97.5) as a Comparative Example, which was also outside that range, gave a fracture toughness value as low as 7.10 MPa√m. Thus, the desired zirconia-based sinter was unable to be obtained from these compositions.

Further, Composition Nos. 1 and 2 as Comparative Examples, which contained no boron (B) component, and Composition No. 5, which contained a boron (B) component in an amount exceeding the range specified in this invention, gave sinters having poor thermal stability as apparent from Table 2, even through these compositions were within the R_2O_3/ZrO_2 molar proportion range specified in this invention.

Furthermore, even when raw-material blends prepared so that the molar proportion of a stabilizer (R_2O_3) to ZrO_2 is within the range specified in this invention and that the additives according to the present invention (a boron compound and Al_2O_3 and/or SiO_2) are within the respective ranges specified in this invention are used, the zirconia-based sinter of the present invention cannot be obtained therefrom when calcination is performed under conditions outside the range of from 500 to 1,200°C or when the specific surface area of the raw material or the conditions for main burning are outside the ranges specified in this invention. For example, in the case of a Comparative Example in which calcination was conducted at 1,400°C, which is outside the range specified in this invention (500 to 1,200°C), and a Comparative Example in which calcination was omitted (see Composition No. 19 in Table 3), the former gave a sinter having a bending strength as extremely low as 11.63 kgf/mm² and the latter gave a sinter having a low fracture toughness value (4.11 MPa√m).

Moreover, Composition No. 9 shown in Table 2 which employed a raw material having a specific surface area of 6 m²/g, which is outside the range specified in this invention (10 m²/g or larger for the oxide-mixing method), gave a sinter having a low bending strength and poor thermal stability. Further, with respect to the Comparative Examples in which sintering (main burning) was conducted at 1,700°C and 1,200°C (see Composition No. 21 in Table 3), which are outside the range specified in this invention (1,300 to 1,650°C), the sinter obtained from the former through high-temperature sintering had undergone a reaction with the burning table, while the sinter obtained from the latter through low-temperature sintering had a bending strength as extremely low as 2.09 kgf/mm². Thus, both compositions failed to give the high-toughness zirconia-based sinter desired in this invention.

[EXAMPLE 2 (including COMPARATIVE EXAMPLES)]

A raw material obtained by the neutralizing coprecipitation method and containing either 1-2.5% by mole Y_2O_3 or 1.8% by mole Yb_2O_3 was mixed with weighed amounts of B_2O_3, Al_2O_3, and SiO_2 so as to result in the compositions (Composition Nos. 27 to 47) shown in Table 4 given below. Using ion-exchanged water as solvent, each mixture was

kneaded with a rubber-lined ball mill employing ZrO_2-based balls. Drying was then conducted.

TABLE 4

Composition						
Composition No.	Kind of stabilizer	R_2O_3/ZrO_2 (mol%)	Al_2O_3 (mol%)	SiO_2 (mol%)	B_2O_3 (mol%)	Remarks
27	Y_2O_3	1.8/98.2	0	0	0	Comparative Example
28	"	"	1	0.3	0	Comparative Example
29	"	"	0	0	2	Example
30	"	"	0	0	8	Example
31	"	"	0	0	12	Comparative Example
32	"	"	1	0	1	Example
33	"	"	0	0.3	1	Example
34	"	"	1	0.3	0.05	Example
35	"	"	1	0.3	1	Example
36	"	"	1	0.3	12	Comparative Example
37	"	"	0.1	0.3	1	Example
38	"	"	5	0.3	1	Example
39	"	"	10	0.3	1	Comparative Example
40	"	"	1	1.5	1	Example
41	"	"	1	3	1	Comparative Example
42	"	1.5/98.5	1	0.3	1	Example
43	"	1.3/98.7	1	0.3	1	Example
44	"	1/99	1	0.3	1	Comparative Example
45	"	1.9/98.1	1	0.3	1	Example
46	"	2.5/97.5	1	0.3	1	Comparative Example
47	Yb_2O_3	1.8/98.2	1	0.3	1	Example

Subsequently, calcination was conducted at the temperatures shown in Tables 5 and 6 given below (provided that the Composition No. 45 indicated by "Calcination temperature: 0°C" in Table 6 was not calcined). The calcined powders obtained were pulverized with the same ball mill as that used above for kneading, to such degrees as to result in the specific surface areas shown in Tables 5 and 6. An acrylic copolymer resin was added in an amount of 3% by weight, and spray granulation was conducted. The resulting powders were subjected to CIP molding at a pressure of 1,000 kgf/cm^2, followed by main burning at the temperatures shown in Tables 5 and 6.

Each zirconia-based sinter obtained was examined for "three-point bending strength," "Vickers hardness," "fracture toughness value," and "thermal stability" by the evaluation methods shown in Example 1 given above. The results thereof

are shown in Tables 5 and 6.

TABLE 5

Production Conditions and Properties

Composition No.	Calcination temperature (°C)	Specific surface area (m^2/g)	Main burning temperature (°C)	Average crystal grain diameter (μm)	Crystalline phase	Bending strength (kgf/mm^2)	Vickers hardness, hardness symbol: HV10	Fracture toughness value MPa√m	Thermal stability	Remarks
27	1000	8	1450	0.7	M+T	42.22	813	4.49	poor	Comparative Example
28	1000	8	1450	0.7	M+T	115.43	1125	12.04	poor	Comparative Example
29	1000	8	1450	0.8	M+T	120.21	1191	11.77	good	Example
30	1000	8	1400	0.6	M+T	117.31	1020	12.54	good	Example
31	1000	8	1450	0.8	M+T	110.16	1023	10.32	poor	Comparative Example
32	1000	8	1450	0.7	M+T	131.30	1150	12.19	good	Example
33	1000	8	1450	0.7	M+T	115.27	1089	10.98	good	Example
34	1000	8	1450	0.7	M+T	112.25	1130	12.14	good	Example
35	1000	8	1450	0.7	M+T	130.96	1092	12.27	good	Example
	1000	3	1450	1.0	M+T	31.78	-	-	poor	Comparative Example
	1000	25	1350	0.6	M+T	108.78	1021	13.21	good	Example
36	1000	8	1400		microcracks were present in the sinter					Comparative Example
37	1000	8	1500	0.7	M+T	117.87	1040	12.43	good	Example
38	1000	8	1450	0.7	M+T	127.72	1245	11.01	good	Example
39	1000	8	1500	0.9	M+T	120.13	1322	6.23	good	Comparative Example
40	1000	8	1450	0.7	M+T	107.60	1095	12.02	good	Example
41	1000	8	1450	0.8	M+T	89.55	1071	10.54	poor	Comparative Example
42	800	10	1450	0.6	M+T	117.85	1043	11.70	good	Example
43	800	10	1450	0.5	M+T	109.20	1015	10.80	good	Example
44	800	10	1450			unsintered				Comparative Example

[note] crystalline phase M: monoclinic phase, T: tetragonal phase

TABLE 6

Production Conditions and Properties

Composition No.	Calcination temperature (°C)	Specific surface area (m^2/g)	Main burning temperature (°C)	Average crystal grain diameter (μm)	Crystalline phase	Bending strength (kgf/mm^2)	Vickers hardness, hardness symbol: HV10	Fracture toughness value MPa√m	Thermal stability	Remarks
45	1000	8	1450	0.7	M+T	141.70	1190	13.20	good	Example
	500	12	1450	0.6	M+T	140.92	1202	13.49	good	Example
	1200	5	1450	0.7	M+T	129.31	1123	11.99	good	Example
	1400	2	1450	0.8	M+T	20.39	-	-	poor	Comparative Example
	0	10	1450	0.7	M+T	72.50	980	5.21	good	Comparative Example
46	1000	8	1450	0.9	T	139.00	1209	7.01	good	Comparative Example
47	1000	8	1450	0.7	M+T	131.20	1050	12.54	good	Example
	800	30	1350	0.6	M+T	121.25	1018	13.60	good	Example
	800	8	1700	reaction occurred with the burning table						Comparative Example
	1000	8	1200	0.5	M+T	8.72	-	-	poor	Comparative Example

[note] crystal phase M: monoclinic phase, T: tetragonal phase

From Tables 5 and 6 given above, it is understood that zirconia-based sinters not only showing high strength and a high fracture toughness value but having satisfactory thermal stability are obtained in Example 2, in which the molar

proportion of a stabilizer (R_2O_3) to ZrO_2 is within the range specified in this invention and the compositions contain a boron compound in a given range (or a boron compound in a given range and Al_2O_3 and/or SiO_2).

In contrast, the zirconia-based sinter of the present invention cannot be obtained from the compositions which are outside at least one of the aforementioned given ranges specified in this invention, or from the compositions containing no boron (B) component. For example, Composition No. 44 (R_2O_3/ZrO_2=1/99) as a Comparative Example, which was outside the range "R_2O_3/ZrO_2=1.3/98.7 to 2/98, excluding 2/98" specified in this invention, did not sinter because of the too small stabilizer (Y_2O_3) amount, and Composition No. 46 (R_2O_3/ZrO_2=2.5/97.5) as a Comparative Example, which was also outside that range, gave a fracture toughness value as low as 7.01 MPa√m. Thus, the desired zirconia-based sinter was unable to be obtained from these compositions.

Further, Composition Nos. 27 and 28 as Comparative Examples, which contained no boron (B) component, and Composition No. 31, which contained a boron (B) component in an amount exceeding the range specified in this invention, gave sinters having poor thermal stability as apparent from Table 5, even through these compositions were within the R_2O_3/ZrO_2 molar proportion range specified in this invention.

Furthermore, even when raw-material blends prepared so that the molar proportion of a stabilizer (R_2O_3) to ZrO_2 is within the range specified in this invention and that the additives according to the present invention (a boron compound and Al_2O_3 and/or SiO_2) are within the respective ranges specified in this invention are used, the zirconia-based sinter of the present invention cannot be obtained therefrom when calcination is performed under conditions outside the range of from 500 to 1,200°C or when the specific surface area of the raw material or the conditions for main burning are outside the ranges specified in this invention. For example, in the case of a Comparative Example in which calcination was conducted at 1,400°C, which is outside the range specified in this invention (500 to 1,200°C), and a Comparative Example in which calcination was omitted (see Composition No. 45 in Table 6), the former gave a sinter having a bending strength as extremely low as 20.39 kgf/mm^2 and the latter gave a sinter having a low fracture toughness value (5.21 MPa√m).

Moreover, Composition No. 45 shown in Table 6 which employed a raw material having a specific surface area of 2 m^2/g, which is outside the range specified in this invention (3 m^2/g or larger for the chemical-synthesis method), gave a sinter having a low bending strength and poor thermal stability. Further, with respect to the Comparative Examples in which sintering (main burning) was conducted at 1,700°C and 1,200°C (see Composition No. 47 in Table 6), which are outside the range specified in this invention (1,300 to 1,650°C), the sinter obtained from the former through high-temperature sintering had undergone a reaction with the burning table, while the sinter obtained from the latter through low-temperature sintering had a bending strength as extremely low as 8.72 kgf/mm^2. Thus, both compositions failed to give the zirconia-based sinter desired in this invention.

[EXAMPLE 3 (including COMPARATIVE EXAMPLES)]

Raw materials prepared by the method described in Example 1 given above (which were Composition Nos. 2, 9, and 20 in Table 1; calcination temperature: 1,000°C, specific surface area: 10 m^2/g) were used and molded into such a shape as to give, through sintering, a ball having a diameter of 1/2 inch. These moldings were burned at 1,500°C to produce grinding media.

Using the grinding media obtained, an abrasion test was performed. In the abrasion test, 3.6 kg of a sample medium was placed in a 2-liter alumina-based ball mill pot together with 800 cc of water and a fused alumina powder (#325), and the pot was rotated at a rotational speed of 100 rpm for 48 hours to measure the resulting decrease of the medium weight through the test. From this decrease, the wear rate of the grinding medium used was determined. Further, the wear rate was determined after conducting a hot-water test, that is, after a 200-hour aging test in 200°C hot water placed

in an autoclave. The results thereof are shown in Table 7.

TABLE 7

Grinding Medium Properties						
Composition No.	Average crystal grain diameter (μm)	Bulk density (g/m³)	Crystalline phase	Wear rate (%)	Wear rate after hot-water test (%)	Remarks
2	0.7	6.03	M+T	0.38	8.20	Comparative Example
9	0.7	6.03	M+T	0.38	0.38	Example
20	0.9	6.06	T	0.52	0.52	Comparative Example

As apparent from Table 7 given above, the grinding part material (grinding medium) employing a zirconia-based sinter of the present invention (Composition No. 9) was ascertained to have a low wear rate and excellent thermal stability and, in particular, to undergo little change in wear rate through the hot-water test.

[EXAMPLE 4 (including COMPARATIVE EXAMPLES)]

Raw materials prepared by the method described in Example 1 given above (which were Composition Nos. 2, 9, and 20 in Table 1; calcination temperature: 1,000°C, specific surface area: 10 m^2/g) were used. Thereto were added weighed amounts of Pr_6O_{11} and Er_2O_3 as colorants so as to result in the compositions shown in Table 8. Using ion-exchanged water as solvent, each mixture was kneaded with a rubber-lined ball mill employing ZrO_2-based balls. Drying was then conducted. In order to produce compounds for injection molding, a resin and a wax were added to the resulting compositions serving as starting materials, and the mixtures each was heated and kneaded with a heated kneader and then pelletized for stable feeding to an injection molding machine. Subsequently, the above-described compounds (pellets) each was introduced into an "injection molding machine having a mold designed to have the given desired shape of a bracket for dentition correction" and molded. These moldings were heated at a temperature of about 350°C to decompose and eliminate the resin contained in the compounds, and were then sintered at 1,500°C.

Surfaces of the thus-obtained brackets for dentition correction were polished. The brackets were examined for "Vickers hardness (JIS R1610)" and "fracture toughness value (JIS R1607)" and evaluated for "thermal stability" by the same methods as in Example 1 given above. Further, the brackets were also examined for "three-point bending strength." The results thereof are shown in Table 8. The test pieces used in examining the "three-point bending strength" were produced by injection molding under the same conditions as for the formation of the bracket shape for dentition correction so that

the samples had the shape according to Testing Method for Bending Strength of Fine Ceramics (JIS R1601).

TABLE 8

Properties of Bracket for Dentition Correction

Composition No.	Amount of colorant (mol%) Pr_6O_{11}	Amount of colorant (mol%) Er_2O_3	Average crystal grain diameter (μm)	Porosity (%)	Bending strength (kgf/mm²)	Vickers hardness [HV10]	Fracture toughness value MPa√m	Color tone	Thermal stability	Remarks
2	0.0005	0.08	0.7	0.2	100.41	1070	11.95	ivory+transparent appearance	poor	Comparative Example
9	0.00009	0.007	0.7	0.2	117.38	1072	11.97	whitish light yellow	good	Comparative Example
	0.0001	0.01	0.7	0.2	118.07	1078	12.31	ivory+transparent appearance	good	Example
	0.0005	0.08	0.7	0.2	118.72	1065	12.21	ivory+transparent appearance	good	Example
	0.002	0.2	0.7	0.2	119.45	1080	12.14	ivory+transparent appearance	good	Example
	0.0025	0.25	0.7	0.2	117.92	1081	12.09	brownish ivory	good	Comparative Example
20	0.0005	0.08	0.9	0.1	115.27	1180	6.20	ivory+transparent appearance	good	Comparative Example

As apparent from Table 8, it was ascertained that the zirconia-based brackets for dentition correction of the present invention show excellent values of sinter properties in all of three-point bending strength, Vickers hardness, and fracture toughness value as in Example 1, even when compared with zirconia ceramic materials on the market, and that with

respect to thermal stability, the surfaces of the brackets undergo no change in quality. Thus, it was suggested that the brackets of this invention are utterly satisfactory when disinfection conditions or conditions for ordinary use in the mouth are taken in account.

Further, in the case where the addition amounts of Pr_6O_{11} and Er_2O_3 were smaller than the amounts specified in this invention, the bracket was too white (assumed a whitish light yellow color). In contrast, in the case of too large colorant amounts, the bracket was darker than teeth (assumed a brownish ivory color). Thus, in either case, the bracket material, when bonded to teeth, gave an unnatural feeling and were aesthetically undesirable because it differed in appearance and color tone from the teeth.

POSSIBILITY OF INDUSTRIAL APPLICATION

The zirconia-based sinter according to the present invention is characterized as comprising ZrO_2 as the main component, a rare earth metal oxide (R_2O_3) in a given range, and a boron compound in a given range (or a boron compound in a given range and Al_2O_3 and/or SiO_2 in a given range). Due to this, a zirconia-based sinter excellent in thermal stability and fracture toughness properties can be provided.

Further, the process according to the present invention for producing a zirconia-based sinter is characterized as comprising preparing a raw-material blend by a chemical synthesis method or the oxide-mixing method so as to result in a given raw-material composition, calcining the blend at a given temperature (500 to 1,200°C), subjecting the calcination product to a pulverization step to obtain a raw-material powder having a specific surface area (which is 3 m^2/g or larger when the blend was obtained by a chemical synthesis method, or is 10 m^2/g or larger when the blend was obtained by the oxide-mixing method), subsequently molding the raw-material powder, and then sintering the molding at a given temperature (1,300 to 1,650°C). According to this process of the present invention, sintering can be conducted at a relatively low temperature. In addition, the present invention brings about an effect that a zirconia-based sinter having exceptionally high toughness and excellent thermal stability can be produced not only through production by a chemical synthesis method but through the oxide-mixing method, which is a relatively inexpensive production method.

Moreover, according to the present invention, it is possible to provide a zirconia-based sinter which has various properties including high toughness, lubricity, heat-insulating properties, thermal expansion characteristics, and oxygen ion conductivity and which, taking advantage of these properties, is expected to be industrially used in wide application fields. It is also possible to provide at low cost a zirconia-based sinter having excellent thermal stability and exceedingly high toughness. Thus, the industrial usefulness thereof is extremely high.

Furthermore, according to the grinding part material employing a zirconia-based sinter having the composition according to the present invention, a grinding part material having high strength and high toughness, excellent in wear resistance and thermal stability, and having a high grinding efficiency is provided.

The grinding part material of the present invention having such properties is industrially extremely useful as a grinding part material, e.g., a lining material or a grinding medium, for use in various grinding apparatus for the dry or wet fine pulverization of particles of ceramics, metals, organic polymers, etc. Moreover, according to the bracket material for dentition correction employing a zirconia-based sinter having the composition according to the present invention, a bracket material for dentition correction which has high strength, high hardness, and high toughness and is excellent in aesthetic property during use and thermal stability can be provided.

Claims

1. A zirconia-based sinter comprising ZrO_2 as the main component, one or more rare earth metal oxides selected from the group consisting of Yb_2O_3, Er_2O_3, Ho_2O_3, Y_2O_3, and Dy_2O_3, and a boron compound, characterized in that the content of boron components is from 0.05 to 8% by mole in terms of boron oxide (B_2O_3), the molar proportion of the rare earth metal oxides (R_2O_3) to ZrO_2 (R_2O_3/ZrO_2) is from 1.3/98.7 to 2/98, excluding 2/98, and the crystal grains obtained consist mainly of a mixed phase made up of tetragonal crystals and monoclinic crystals.

2. A zirconia-based sinter comprising ZrO_2 as the main component, one or more rare earth metal oxides selected from the group consisting of Yb_2O_3, Er_2O_3, Ho_2O_3, Y_2O_3, and Dy_2O_3, a boron compound, and Al_2O_3 and/or SiO_2, characterized in that the content of boron components is from 0.05 to 8% by mole in terms of boron oxide (B_2O_3), the molar proportion of the rare earth metal oxides (R_2O_3) to ZrO_2 (R_2O_3/ZrO_2) is from 1.3/98.7 to 2/98, excluding 2/98, the content of Al_2O_3 is from 0.1 to 5% by mole and/or the content of SiO_2 is from 0.05 to 1.5% by mole, and the crystal grains obtained consist mainly of a mixed phase made up of tetragonal crystals and monoclinic crystals.

3. The zirconia-based sinter as claimed in claim 1 or 2, which is characterized in that the boron compound is boron oxide, boron nitride, boron carbide, or a compound of any of the elements shown in claim 1 or 2 (Zr, Al, Si, Yb, Er, Ho, Y, and Dy) with boron (B).

4. A process for producing a zirconia-based sinter comprising ZrO_2 as the main component, one or more rare earth metal oxides (R_2O_3) selected from the group consisting of Yb_2O_3, Er_2O_3, Ho_2O_3, Y_2O_3, and Dy_2O_3, and a boron compound [or a boron compound and Al_2O_3 and/or SiO_2], characterized as comprising the steps of:

(1) preparing a raw-material blend by a chemical synthesis method, such as the neutralizing coprecipitation method, the hydrolytic method, the alkoxide method, or the like, or by the oxide-mixing method so that the blend has such a raw-material composition that the molar proportion of the rare earth metal oxides (R_2O_3) to ZrO_2 (R_2O_3/ZrO_2) is from 1.3/98.7 to 2/98, excluding 2/98, and that the content of the boron compound is from 0.05 to 8% by mole in terms of boron oxide (B_2O_3) [or that the content of the boron compound is from 0.05 to 8% by mole in terms of boron oxide (B_2O_3) and the content of the Al_2O_3 is from 0.1 to 5% by mole and/or the content of the SiO_2 is from 0.05 to 1.5% by mole],
(2) calcining the raw-material blend at 500 to 1,200°C,
(3) pulverizing the calcination product to such a degree as to result in a specific surface area of 3 m^2/g or larger when the raw-material blend was obtained by a chemical synthesis method or of 10 m^2/g or larger when the raw-material blend was obtained by the oxide-mixing method,
(4) molding the powder obtained by pulverization, and
(5) sintering the molding at 1,300 to 1,650°C.

5. A grinding part material constituted of the zirconia-based sinter as claimed in claim 1, 2, or 3 or of a zirconia-based sinter obtained by the process as claimed in claim 4, wherein the grinding part material comprises the zirconia-based sinter as claimed in claim 1, 2, or 3 or the zirconia-based sinter obtained by the process as claimed in claim 4 which is characterized in that the sinter has an average grain diameter of 2 μm or smaller and a bulk density of 5.8 g/cm^3 or higher and is less apt to deteriorate in long-term use at a temperature of 100 to 300°C in the air or in water and steam.

6. A bracket material for dental correction constituted of the zirconia-based sinter as claimed in claim 1, 2, or 3 or of a zirconia-based sinter obtained by the process as claimed in claim 4, characterized in that the bracket material for dental correction constituted of the zirconia-based sinter as claimed in claim 1, 2, or 3 or of the zirconia-based sinter obtained by the process as claimed in claim 4 contains from 0.0001 to 0.002% by mole Pr_6O_{11} and from 0.01 to 0.2% by mole Er_2O_3 as colorants for enhancing the aesthetic properties of the sinter, and that the sinter has an average grain diameter of 2 μm or smaller and a porosity of 1% or lower and is less apt to deteriorate in long-term use at a temperature of 100 to 300°C in the air or in water and steam.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP95/00762

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl[6] C04B35/486, A61C7/14, B02C17/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl[6] C04B35/48, A61C7/14, B02C17/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 4-280864, A (HOYA Corp.), October 6, 1992 (06. 10. 92) & DE, 4207179, A & US, 5219805, A & US, 5263858, A	1 - 6
A	JP, 2-21857, A (Sadoun Mikael), January 24, 1990 (24. 01. 90) & FR 2627377, A & US, 5011403, A & DE, 68919724, E	1 - 6
A	JP, 3-237059, A (Mitsubishi Materials Corp.), October 22, 1991 (22. 10. 91) (Family: none)	1 - 6
A	JP, 63-252963, A (Ibiden Co., Ltd.), October 20, 1988 (20. 10. 88) (Family: none)	1 - 6
A	JP, 4-349172, A (Nissan Chemical Industries, Ltd.), December 3, 1992 (03. 12. 92) & AU, 633445, B & US, 5279995, A, & DE, 69102028, E	1 - 6

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
July 18, 1995 (18. 07. 95)	August 8, 1995 (08. 08. 95)

Name and mailing address of the ISA/	Authorized officer
Japan se Patent Office	
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP95/00762

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PA	JP, 6-239662, A (Shinagawa Refractories Co., Ltd.), August 30, 1994 (30. 08. 94) (Family: none)	1 - 6

Form PCT/ISA/210 (continuation of second sheet) (July 1992)